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Introduction

Polycyclic aromatic hydrocarbons (PAH) are a common pollutant created by natural (forest fires) or anthropogenic sources, such as incomplete combustion in engines (vehicular traffic) or incinerators (1). Many PAHs are known or suspected carcinogens and also have mutagenic properties and endocrine disrupting effects (2).

Although most atmospheric PAHs are measured using high-volume sample collection on filters, a convenient way of monitoring these pollutants is through plant matrices, such as pine needles that act as passive samplers. The needles are covered with a lipid-rich cuticle that absorbs the pollutants (1). Evergreens are especially useful because they continue to accumulate pollutants during the winter (3).

In order to use plants as monitors, a method to extract the PAHs must be used. Ultrasonication is a method that leaches the PAHs from the needles and into the solvent. The sonication agitates the pine needles and produces increased temperatures, which further abet the efficiency of the solvents' extraction. This rapid method can be applied to batches of samples. The procedure is followed by a cleanup step (4).

Experimental

- Sample Collection
  - Samples of third year pine needles were collected with scissors and placed in an amber bottle.
  - Samples were kept in the dark due to PAH photosensitivity.
  - Samples were allowed to air dry prior to extraction.
- Extraction
  - Needles were chopped into 2 mm size bits with a coffee grinder.
  - Amber bottles were filled with 5.00 g of chopped needles and spiked with 1000 ng of deuterated standard.
  - 30.0 mL of solvent was added to sample. Sample was sonicated three times after being left to soak overnight.
  - All extracts were combined in a round bottom flask and rotovapped down to 2 mL.
- Clean up
  - Cartridges were prepared with 2.5 g of Florisil and 0.5 g of Na_2SO_4 and conditioned with 30 mL of solvent.
  - The extract was loaded onto the column and eluted with solvent.
  - The filtrate was then blown down and stored in vials.
- Analysis
  - Samples and standards were spiked with a 1 ppm solution before analysis
  - Analysis was ran under SIM.

References

(1) Nicola, Flavia De; Chemosphere 61 (2005) 432-440
(2) Ratola, Nuno; Journal of Chromatography A, 1114 (2006) 198-204
(3) Prajapati, Santosh Kumar; Environmental Pollution 151 (2008) 543-548
(4) McGowin, A.E., "Polycyclic aromatic hydrocarbons" in Chromatographic Analysis of the Environment. CRC Press, UK, 2005
(5) Srogi, K. "Monitoring of Environmental Exposure to Polycyclic Aromatic Hydrocarbons: A Review". Environ Chem Lett (2007) 5:169-195

Table 1 Analytes, Internal Standard, Surrogates

Peak #	Compound Name	CAS no.	Molecular wt.	Retention Time
1	Naphthalene[v]	[91-20-3]	128	7.629
2	Naphthalene-d8*	[1146-65-2]	136	7.589
3	Acenapthalene[v]	[83-32-9]	152	11.49
4	Acenaphthene-d10*	[15067-26-2]	164	11.613
5	Acenaphthene[v]	[208-96-8]	153	11.683
6	Fluorene[v]	[86-73-7]	166	12.892
7	Phenanthrene-d10*	[1517-22-2]	188	15.246
8	Phenanthrene[v]	[85-01-8]	178	15.303
9	Anthracen[v]e	[120-12-7]	178	15.421
10	Fluoranthene[v]	[206-44-0]	202	18.551
11	Pyrene[v]	[129-00-0]	202	19.165
12	p-terphenyl`	[92-94-4]	230	19.808
13	Benza[a]anthracene[v]	[56-55-3]	228	23.008
14	Chrysene-d12*	[1719-03-5]	240	23.067
15	Chrysene[v]	[218-01-9]	228	23.152
16	Benzo[b]fluoranthene[v]	[205-99-2]	252	27.125
17	Benz[a]pyrene[v]	[50-32-8]	252	27.220
18	Benzo[k]fluoranthene[v]	[207-08-9]	252	28.359
19	Perylene-d12*	[1520-96-3]	264	28.811
20	Indeno[1,2,3-cd]pyrene[v]	[193-39-5]	276	32.697
21	Dibenzo[a,h]anthracene[v]	[53-70-1]	278	32.821
22	Benzo[ghi]perylene[v]	[191-24-2]	276	33.619

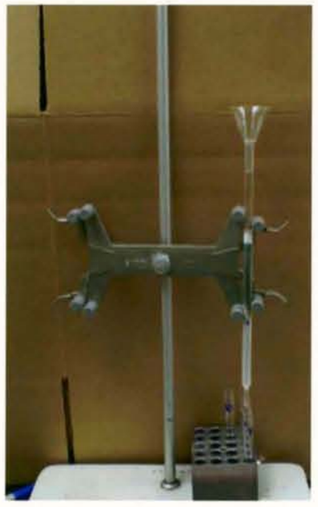
Legend
* Deuterated Standard
` Interdnal Standard
v PAH

Pictures

Figure 1

Figure 2

Figure 3



GC Settings

Table 2 GC/MS Column Settings

Column Length:	30.00 m
Column Diameter:	0.320 mm
Gas:	He
Vacuum Compensation:	On

Table 3 Oven Programming

Initial Temperature:	80 C
Intial Time:	1.00 min

Level	Rate (C/minute)	Final Temperature (C)	Final Time (min)
1	10	190	0
2(A)	8	250	0
3(B)	4	320	0
Next Run Time:	37 minutes		

Table 4 Inlet Purge Settings

Inlet Purge	Init Value	On Time	Off Time	Splitless Injection
A	Off	0.50	5.00	Yes
B	Off	0.50	0.00	No

Figure 4

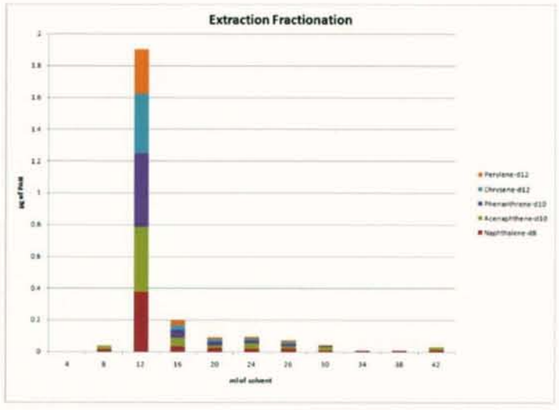


Table 5 µg of PAH in Each Fraction

ml of Solvent	4	8	12	16	20	24	26	30	34	38	42
Naphthalene-d8 µg	0	0.013442	0.373655	0.033393	0.021435	0.020162	0.019681	0.008383	0.006911	0.008273	0.01246
Acenapthene-d10 µg	0	0.025515	0.409987	0.052328	0.017662	0.032771	0.012698	0.020458	0	0	0.01601
Phenanthrene-d10 µg	0	0	0.464331	0.049994	0.02385	0.018839	0.018158	0.008221	0	0	0
Chrysene-d12 µg	0	0	0.373745	0.031792	0.015289	0.011771	0.011417	0.00279	0	0	0
Perylene-d12 µg	0	0	0.278218	0.029684	0.012999	0.010501	0.010968	0.002804	0	0	0

Data and Results

Figure 5

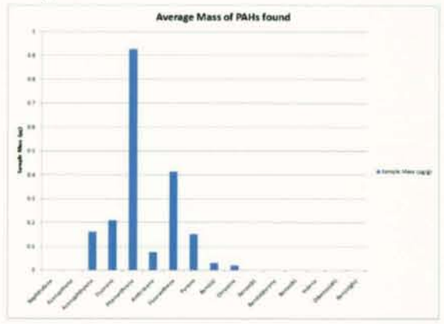


Table 6 Concentration of PAHs in Pine Needles

Analyte	Sample A(µg/g)	Sample B(µg/g)	Average(µg/g)
Naphthalene	4.12042E-05	0	2.06021E-05
Acenapthene	0	0	0
Acenaphthylene	0.143652209	0.176965365	0.160308787
Fluorene	0.190416537	0.226809904	0.20861322
Phenanthrene	0.878491698	0.975596	0.927043849
Anthracene	0.073089272	0.076943617	0.075016445
Fluoranthene	0.379905236	0.445438893	0.412672065
Pyrene	0.144134669	0.156893657	0.150514163
Benz(a)	0.027250721	0.032378731	0.029814726
Chrysene	0.012496953	0.025256556	0.018876754
Benzo(b)	0	0	0
Benz(a)pyrene	0	0	0
Benzo(k)	0	0	0
Indeno	0	0	0
Dibenzo(ah)	0	0	0
Benzo(ghi)	0	0	0
	Total		1.982880612

Conclusion

Phenanthrene was exceptionally high, 927 ng/g, in the tree located at a busy urban intersection between two major roads and along a railroad track. The total PAH concentration (Σ_{EPA16}) was 1982 ng/g. This is comparable to pine needles concentrations in typical urban areas that range from 800-1600ng/g(5). A high level of phenanthrene indicates the source is vehicle exhaust.

Improvements to the method will include increasing recovery and analyzing a larger sample.